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Volume 3. Leather Tannery Sludges

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LAND TREATMENT FIELD STUDIES

Volume 3. Leather Tannery Sludges

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This report presents the results of field measurements and observations of a land treatment site which incorporates sludge generated from air pollution control scrubbers of a leather tannery operation. The waste contains a high concentration of nitrogen, and has other soil-amending qualities so that for the past 20 years, the site has received tannery wastes to improve growth of crops. These include corn, wheat, and hay. The waste also contains high concentrations of sodium, chromium and organic species. The site was sampled once and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analyses were conducted on the waste and soil/waste mixture; inorganic analysis was performed on plant samples.

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FOREWORD

The U.S. Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimonies to the deterioration of our natural environment. The complexity of that environment and the interplay of its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution; and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems to prevent, treat, and manage wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, to preserve and treat public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research and provides a most vital communications link between the researcher and the user community.

This report provides the results of a field study investigation of one of six sites receiving industrial waste sludges by land cultivation. The purpose of the study was to identify and verify parameters which lead to environmental acceptability of the waste, and to recommend research needs for establishing guidelines and criteria for land cultivation.

Francis T. Mayo, Director
Municipal Environmental Research
Laboratory

ABSTRACT

This report presents the results of field measurements and observations of a land treatment site which incorporates sludge generated from air pollution control scrubbers of a leather tannery operation. The waste contains a high concentration of nitrogen, and has other soil-amending qualities so that for the past 20 years, the site has received tannery wastes to improve growth of crops. These include corn, wheat, and hay. The waste also contains high concentrations of sodium, chromium and organic species. The site was sampled once and observations were made on the type and amount of waste handled, site characteristics, and management procedures for waste application and monitoring. Organic and inorganic analyses were conducted on the waste and soil/waste mixture; inorganic analysis was performed on plant samples.

The area of the site sampled had received only one waste application and therefore results may not be indicative of the site as a whole. A significant increase (20 fold) of chromium content in the application soil was observed; however, no significant increase was identified in the crop samples grown on the application area. A monitoring program is recommended to identify any development of potential problems cited in this report.

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SECTION 1

INTRODUCTION

Land treatment is the application and incorporation of solid or semisolid waste into surficial soils. Other terms used to describe this practice include land cultivation, refuse farming, land spreading, soil farming and soil incorporation. The term land application, on the other hand, usually refers to irrigation of surficial soil with wastewater. Land treatment is essentially a physical/chemical/biological waste treatment method that utilizes the natural capacity of the soil system to aerobically degrade, assimilate and immobilize certain waste constituents.

At every land treatment site, there is a dynamic balance of decomposition attenuation and migration of waste constituents. The extent to which any one of these mechanisms occurs depends on the waste character, site character and cultivation procedures.

A land treatment site should provide decomposition of the organic constituents applied and incorporated. The migration of soluble constituents from a landfarming site should be within environmentally acceptable concentrations for the receiving media, particularly ground and surface waters. The attenuation of remaining constituents over the design life of the site should not lead to a build up of total concentrations that could harm the soil structure, cause phytotoxicity, or lead to excessive concentrations in the food web through bioaccumulation.

From the above discussion, it is evident that specific site characteristics and waste characteristics together are key to achieving environmentally optimal use of surficial soils in waste treatment. Equally important (although not evident) is the management of the land cultivation operation; no matter how optimal conditions may be for degradation/attenuation of waste, some sites can be overloaded. Management of a site can be viewed as the means through which desired waste treatment conditions are maintained.

OBJECTIVES

The objective of this project was to identify parameters which contribute to (or affect) the environmental acceptability of land treatment of a sludge from a leather tannery . The parameters are classified by waste characteristics (e.g., percent solids, salt content), site characteristics (e.g., topography, climate) and land treatment management procedures (e.g., soil aeration, frequency of waste application). Environmental acceptability was determined by comparing concentrations of waste constituents in the application soils and control area soils, and by assessment of the potential for environmental contamination due to a combination of waste, site and management parameters.

DESCRIPTION OF THE SITE

The identity of this site is protected by a confidentiality agreement included as part of the contract for this study. The farm which includes wheat, hay, and cornfields and an orchard, has had applications of a variety of leather tannery wastes since 1961.

Waste Characteristics

Until 1967, a variety of leather tannery facility wastes (SIC Code 3111) were applied at the farm. In recent years, a scrubber sludge from an air pollution system at the facility has been the major waste land treatment at the site. The scrubber sludge contains 6% solids, (94% water) when delivered to the site. Waste constituents include: nitrogen, sodium, chromium, and organic species. High nitrogen levels (8.1% dry weight basis) make the waste a good nitrogen source for farming soils. In addition, the waste is a good soil conditioner and improves water retention in the site soils. Both state officials and the land treatment site management view the waste as a soil amendment.

Site Characteristics

The land treatment site is owned by a local farmer and leased to the farm operator. Site topography consists of rolling hills with slopes in the range of 3% to 8%. Wheat, corn and hay are grown at the farm. In addition there is a small orchard on the site.

The historic seasonally high ground water table at the site is one and a half to three feet below grade. Field visits revealed a very shallow, possibly intermittent, pond in the northeast corner of the farm. Average annual precipitation at the site area is 41 inches and is evenly distributed throughout the year. The annual frost-free period ranges from 184 to 241 days. Average temperature ranges from a daily maximum of ∿86°F in July to a daily minimum of ∿26°F in January. General characteristics of site topography, groundwater, surface water, and climate are summarized in Table 1.

Soils in the vicinity of the site may be generally classified as silt loams, a number of different silt loam soil series exist in this area. Most soils on the treatment site have been classified as deep, well-drained silt, loam soils that grade to fine sandy loam in the substratum (44 + inches). The content of coarse fragments, which may be 10 to 20% in surface layers, increases with depth in the substratum and predominates at about 80 inches. Other soil properties are a near-neutral pH and a moderately high CEC. These characteristics usually represent a good assimilative capacity for metals such as cadmium, zinc, copper, etc., and suitable conditions for microbial degradation processes.

In one area bedrock is reported to lie one and a half to three feet below grade. In another area a fragipan* evidently exists one and a half to two feet below grade. Either the shallow bedrock or the fragipan could account

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* A fragipan is a dense and brittle pan in soils due to extreme density or compactness; the material is so dense that plant roots cannot penetrate and water moves through it very slowly.

TABLE 1. SELECTED PHYSICAL/CHEMICAL CHARACTERISTICS OF THE SITE

	Published Source*	Data From Site Visit/ Analysis**
I. Soil Conditions		
A. Soil Classification	Silt loam: moderately eroded	-
B. pH Characteristics	6.5-7.0	6.8 (control area)
C. Cation Exchange Capacity (meq/100g soil)	-	10.3-14.2 meq/100g soil (control area)
D. Soil Organic Content (or TOC)	-	TOC: 1.45% dry solids (control area)
E. Water Retention Ability	a) Available water capacity: 0.10 to 0.16 inches per inch of soil b) Permeability: 0.63 to 2.0 inches per hour	-
II. Ground & Surface Water Proximity		
A. Surface Water	a) Small stream ~600 to 1000 feet downslope both south and east b) Small spring/pond ~1000 feet north of sampling area	Same (spring is potable water supply)
B. Ground Water	3 foot depth to seasonal high water table (seasonally, water table may be even higher in spots)	Farm residents have private well
III. Topographic Conditions		
A. General Topography of Vicinity of Site	Rolling hills; 3 to 8% slope, average. Slope indicated as major limitation for farming in this area.	-
B. Topographic Relief of Area Visited	-	Area sampled had gentle slope; < 3%; rest of area more typical of vicinity.
IV. Climatological Conditions		
A. Average Yearly Precipitation	~41 inches (Fairly evenly distributed)	
B. Frost Free Period	~184-241 days (194 day average)	
C. Summer Maximum Temperature	~86° F (July - daily average)	
D. Winter Minimum Temperature	~26° F (Jan/Feb - daily average)	

*Includes information from Soil Conservation Service Personnel & Publications, USGS Surveys and/or State & University Surveys.

**Includes Arthur D. Little, Inc. observations and analyses from site visits, as well as interviews with facility personnel and representatives of waste generators and farms.

for the reported high water table levels of one and a half to three feet below grade

The field sampled is largely located on the more representative deep, well-drained silt loams. Both application and control area soils were of similar consistency. It is possible, however, that the control samples were from the area that is underlain by the shallow fragipan. Hence, control samples might have been more subject to a seasonally decreased hydraulic saturation potential.

Areas adjacent to the site are rural and consist of an ecological mix of deciduous shrub and woodland habitats. Wildlife access to the site is essentially unrestricted by topography or manmade features, and all observations suggest that it can be utilized by a fully representative mix of the terrestrial fauna of the region. This includes, but is not limited to, game birds and mammals of recreational import. The streams and pond system bordering the site are small, and faunal diversity appeared to be limited by flow, which may be intermittent. The site also offers considerable vegetative diversity; the vegetation borders the site and helps mitigate potential erosion problems associated with the hilly setting, and surface runoff into the nearby surface waters.

Land Treatment Site Management

The tannery studied generates approximately 150,000 gallons of waste (wet basis) annually. The waste derives from wet scrubbing of buffing line dusts and is collected in 1000-gallon concrete settling basins. Wastes are transported three miles from the generating facility to the land treatment site in a fiberglass lined, 1300-gallon capacity tank mounted on a truck. The truck is owned by the generator. Two to three loads are transported to the land treatment site weekly.

At the land treatment site, the sludge is deposited through a four-inch gate valve into an unlined holding basin with a capacity of 2,600 cubic feet. The holding basin is located on a hilltop at the site. In the absence of rain, the sludge dries out in the basin in about a week, with water loss being through evaporation and seepage. Occasionally, when the holding basin is full, surface application is made directly to a field. Dewatered sludge has occasionally been excavated from the basin and piled next to it for preapplication storage.

The farming operation at the site dictates when sludge can be applied. Typically, application is in the spring and fall. As noted above, wastes are initially dumped into a small storage basin for dewatering, although they may also, occasionally, be applied directly to open fields. The sludge is periodically removed from the lagoon either by shovelling or by a small farm tractor equipped with a front-end loader and stored in piles. The sludge is then spread on surface soils (by hand or by a small tractor) to depths up to six inches as fields become open, and as part of normal soil preparation. In the past, the dewatered sludge from the basin has also been applied by a manure spreader. Application and incorporation has been carried out by the farmer (which in recent years has been a different individual from the farm owner). No records

have been kept to indicate the volumes and frequency of sludge application for application areas on the site. The farmer estimated application rates were approximately 200,000 gallons/year per acre. In addition to waste applications, chemicals are applied to the soils for pH amendment and fertilizing purposes as part of the agronomic activities.

Management of the landfarming operation is summarized in Table 2, below.

TABLE 2. OPERATIONAL MANAGEMENT

	Plans/Decides Manages/Supervises	Performs	Approves
Storage	W.G.	W.G.	W.G.
Pretreatment	W.G.	W.G.	W.G.
Wastes Mixing	None		
Transport	W.G.	W.G.	W.G.
Applications	LCSO/F	LCSO/F	F
Soil Incorporation	F	F	F
Soil Waste-Amendments	F	F	F
Farming	F	F	F
Monitoring	None		

W.G. = Waste Generator
F = Farmer
LCSO = Land Cultivation Site Owner

The waste generator retains the responsibility for transport of wastes to the farm. Currently, a company employee spends about four hours/week on activities associated with loading and transporting the waste. All other land cultivation activities are the responsibility of the farmer.

Under the present system, there is no communication between the farmer and waste generator concerning waste content, soil or crop conditions, waste volume delivered, etc. This is not surprising, considering the fact that this waste is viewed as a soil amendment. No analysis of the waste, water, or air quality and no bioassays are performed. The soil is analyzed for pH and fertilizer requirements.

SECTION 2

CONCLUSIONS AND RECOMMENDATIONS

In sharp contrast to other land disposal options, land treatment can be managed so that the waste application area need not be irreversibly removed from any other potential practical usage. The basic reason is that plant-soil systems have a natural assimilative capacity for waste constituents. If rates and total quantities of wastes applied are controlled so that the assimilation capacity of the site is not exceeded for any constituent of the waste, no potential future use of the site will be precluded. Assimilative capacity is both chemical specific and site specific. In other words, each chemical constituent of a given waste will be assimilated to a different extent at the same site; and the same chemical constituents will be assimilated differently at different sites.

The conclusions of the present study are limited to the evironmental acceptability of land treatment for air pollution control scrubber sludges from one particular leather finishing plant, at one particular application site. The results cannot be generalized, either to sludges from other plants in the leather tanning industry, or to other potential land treatment sites for the particular air pollution control scrubber sludge investigated. The field study findings do provide insight into the factors that should be considered in the design and operation of a land treatment site to ensure environmental acceptability. The field study results characterize, to the extent possible, actual practices at a land treatment site used for purposes of research. Conditions of waste application were therefore given, and not under the control of the investigators.

CONCLUSIONS

The waste sludge as applied contained about 6% solids and 94% water. Approximately 3000 gallons had been applied for the first time to a one acre area, three months prior to field sampling. The area had subsequently been planted to corn.

Analysis of the dried waste solids showed 1% metals, 44% TOC, 8% nitrogen, less than 1% sulfate and chloride, and 47% undetermined. Of the metals analyzed*, only sodium and chromium showed significantly higher concentrations in the application area than in the control area. Since the sodium content of the waste (1300 μg/g of dried solids) is not excessive relative to calcium and magnesium (1200 and 360 μg/g of dried solids respectively) there is little risk of soil deterioration due to defluocculation and swelling of clay particles. Leaching of sodium salts to groundwater, however, is a distinct possibility, since the seasonally high water table is within three feet of the surface of the site.

*As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V, Zn

The accumulation of chromium in the upper six inches of the application area, calculated from the analytical results, was 1400 kg/ha. This exceeds the estimated assimilation capacity of about 1000 kg/ha** for soils with moderate CEC.

Measured levels of total nitrogen and total organic carbon were also significantly higher in the application area than the control area. The dried waste solids contained 8.1% nitrogen. The quantity applied to the land treatment site prior to sampling had been 137 kg/ha. The measured value of nitrogen in the upper six inches of the application area was 16 kg/ha. It is likely that most of the nitrogen applied had been taken up as a nutrient by the growing corn plants. In general, the nitrogen assimilative capacity of a site planted to corn is considered to be of the order of 200 kg/ha.**

The upper six inches of the application area was found to contain 500 mg/kg of extractable organics, more than two times the level found in the control area (45 mg/kg). Comparison of the mass spectra for extractable organic fractions of the waste and upper six inches of the application area showed the application area to be relatively enriched in aliphatic and aromatic hydrocarbons, and relatively depeleted in polar organics. These organics appeared to have accumulated in the application area, without having undergone substantial decomposition in the three month period between application and sampling. Alternatively, polar organics (C, H, O and C, H. N compounds) in the waste may be selectively degraded or removed from the soil, or simply may not be extracted efficiently from the soil.

Whole corn plants, above soil level, grown in the application area did not show significantly higher metal contents than similar plants grown in the control area. Plant uptake of chromium, which is higher in the application area than in the control area, might be confined to the roots of the corn plants. Roots were not analyzed in this study. On the other hand, if the chromium is present as Cr (III), it is unlikely to be available for plant uptake.

RECOMMENDATIONS

In view of the high level of chromium in the soil and potential impacts on agronomic crops, groundwater, and surface water, a monitoring program should be instituted at the site. Soil, water, and plants (including plant roots) should be routinely analyzed for chromium, sodium, and targeted organic constituents. Careful records should be maintained to facilitate recognition of any developing problems. An evaluation should be conducted of the potential impacts of operating the waste holding pond on a hilltop at the site. To implement these tasks, a more centralized management of the landfarming is necessary. Waste application must be planned and recorded and batch waste characteristics better defined. Good management will minimize potential adverse effects of the landfarming operation.

**M. Overcash and D. Pal, "Design of Land Treatment Systems for Industrial Wastes," Ann Arbor Science, Michigan (1979).

SECTION 3

APPROACH

DATA COLLECTION AND ANALYSIS

Samples of the waste, baseline soil, and soil/waste mixtures were collected and analyzed for inorganic constituents and organic compound classes. Plants were collected and analysed to assess the extent of uptake of inorganic waste constituents.

The analytical protocol involved determining the following classical and inorganic waste parameters: pH, SO_4, and Cl^-, electrical conductivity (EC), cation exchange capacity (CEC), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), As, B, Ca, Cd, Cr, Cu, K, Mg, Mo, Na, Ni, P, Pb, Se, V and Zn. Plasma emission spectroscopy and ion/chromatography were employed for inorganic species.

Analytical techniques employed for organic species included liquid chromatographic separation of organics into aliphatic, aromatic, and polar classes (LC-H, LC-A and LC-X, respectively), total chromatographic organics (TCO) and gravimetric (GRAV) analysis for volatile and non-volatile portions, and high resolution mass spectrometry (HRMS) for sorting classes by hydrogen saturation and heteroatom composition. The sampling and analytical methods are described in detail in the Appendix.

DATA INTERPRETATION

The analytical results from sampling the waste, the site receiving the waste, and a control site were compared to assess, insofar as possible, the relative decomposition, accumulation and migration of inorganic constituents and organic compound classes. The sampling and analytical program used in this study was designed to include sampling and analysis of appropriate control areas at the site so that any apparent concentration changes of waste components in application area samples could be differentiated from background levels. However, during preliminary site visits several factors were identified which would make it difficult to interpret any observed, apparent concentration changes. These factors include the following: an ideal control area was not available at the site; and, the chemical compositions of applied wastes were known to have varied over time.

The existence of many significant sources of uncertainty in the background data on the site made it desirable to provide some additional checks on the validity of the analytical data besides that provided by comparison of

TABLE 3. COMPARISON OF "TYPICAL" ELEMENTAL CONCENTRATION RANGES IN SOILS AND PLANTS WITH CORRESPONDING CONCENTRATION RANGES IN CONTROL AREAS USED IN THIS STUDY

Element	Typical Mean ppm Dry Soil (Range)[1]	Range ppm Dry Soil This Study[2]	Typical Range ppm Dry Plant Wt. Basis	Range ppm in Plant Ash This Study[5]
As	6 (0.1-40)	0.8-16	0.1-5[3]	1-16
B	10 (2-100)	2.1-9.2	5-30[3]	31-620
C	20,000	6,000-29,200	--	--
Ca	13,700 (7,000-50,000)	2,200-13,00	1,000-20,000	23,000-171,000
Cd	0.06 (0.01-0.7)	.3-.7	0.2-0.8[3]	1-4
Cr	100 (5-3,000)	7.9-65	0.2-1[3]	19-140
Cu	20 (2-100)	11-41	4-15[3]	69-290
K	14,000 (400-30,000)	2,300-8,400	20,400[4]	26,000-54,000
Mg	5,000 (600-6,000)	4,000-6,000	500-15,000[4]	14,000-40,000
Mo	2 (0.2-5)	1.7-3.3	0.2-5[3]	14-64
N	1,000 (200-2,500)	464-1,700	--	--
Na	6,300 (750-7,500)	22-440	--	940-10,000
Ni	40 (10-1,000)	9.6-31	10-10,000[4]	7-36
P	650	5,300-10,000	1,000-10,000[4]	17,000-168,000
Pb	10 (2-200)	24-280	0.1-10[3]	29-370
Se	7 (10-25)	0.1-0.5	0.1-2.0[3]	<.1-0.5
V	100 (20-500)	17-50	20-500[3]	3-90
Zn	50 (10-300)	41-110	10-300[3]	270-3,800

1. Bowen, H.G.M., Trace Elements in Biochemistry, Academic Press, Inc., NY, 1966.
2. CTL 0-6" Samples.
3. Allaway, W.H., Agronomic Controls Over the Environmental Cycling of Elements.
4. Berger, K.C., Sun Soil and Survival, University of Oklahoma Press, OK, 1976.
5. CTL Samples.

control and application area sample results. These checks are described below:

Inorganic Analysis

Validation of Control Samples --

The analytical data obtained in this study for control area samples from six land treatment sites are compared in Table 3 to typical concentration ranges found in soils and plants. Comparison of the soils data for the six sites indicates that almost all of the results obtained in this study are within typical concentration ranges. Exceptions are phosphorus (P), which was generally found in concentrations in excess of typical ranges, and sodium (Na) and selenium (Se), which were generally found in concentrations less than typical ranges. The selenium discrepancy may be due to volatilization of that element during the sample preparation procedure used in this study; the reasons for the sodium and phosphorus differences are not clear. Comparison of data on plants is of limited utility for several reasons, viz.: 1) plant uptake is species-specific; 2) uptake by a particular species is dependent on soil conditions; and 3) for the purpose of this study, elemental concentrations in plants have been expressed on an ash weight basis to compensate for the frequently poor physical condition of plants collected in the field. However, if we assume that the ash weight is usually on the order of 10% of the dry weight (the actual mean ash weight for all six control area samples in this study was 8.7% of dry weight), then the majority of results obtained in this study lie within typical ranges encountered in plants on a dry weight basis. In general, comparison of the results for control area samples in this study to typical elemental concentrations ranges in soils and plants suggests that there are no severe biases which would invalidate conclusions from the analytical data presented in this report.

Total Mass of Analyzed Parameters --

The sum of the masses of individual analyzed species in a sample of waste is a fraction of the total waste mass. For instance, if there were no species in the waste solids other than those determined in this study, the sum of all the individual masses should be approximately equal to 100%, depending on the uncertainty associated with the sampling and analytical methods. Inspection of the data presented shows that species determined in this study account for 68% of waste weight. The significance of this observation depends, of course, on the identity of the species that were not determined. Likely candidates are the elements Fe, H, O, Si and Al, all of which could be reasonably expected to occur in significant quantities in wastes of the type included in this study. In any case, consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented in this report.

Definition of Significant Pollutant Increases --

Interpretation requires some judgment about what constitutes a significant change in concentration of a given parameter relative to background levels. To this end, the results for total metals, Total Organic Carbon (TOC), and Total Kjelkahl Nitrogen (TKN), were expressed as ratios of total concentration in the application area to total concentration in the control area (APN/CTL).

Inspection of the data generated from six land treatment sites indicates that three elements - K, Mg, and P - show no significant increases above background, i.e., individual APN/CTL ratios for each of the elements at each site are close to 1.0 indicating that there is little difference in the actual concentrations of each of the elements between the APN and CTL area samples. The relative standard deviations of the mean APN/CTL ratios for these three elements are 33% (K), 9.1% (Mg), and 20% (P). Their mean relative standard deviation is approximately 20%; this number may provide a useful measure of the background variability of elemental concentrations in soils. Thus, for the purpose of this report, it has been assumed that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than $\pm$20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

The results for total metals, TOC and TKN in the wastes from all sites were used along with data obtained from the site owner on waste application rate (i.e., kg waste/acre/yr.) and waste percent solids, to estimate the number of years before one could expect to observe any increase of the elements analyzed in this study. The following assumptions were made:

1. Actual application rates have been the same as those given by the site operator;

2. All the waste generated for land treatment has been applied to the area which we sampled;

3. The waste has been incorporated uniformly into the top 12" of soil over the entire area described in #2; and

4. The waste composition has been constant and identical to that determined in this study.

The resulting estimates are discussed in more detail in chapter 4.

The steps in the procedure used to calculate the years of waste application necessary before one could expect to observe any increase above background were as follows.

Waste Application Rate --

The quantity kilograms of waste solids/acre/year was calculated from data supplied by the waste generator. For certain sites, the waste generator was able to provide an estimate of this quantity directly for other sites, where perhaps only an estimate of the annual volumetric waste generation rate was available, this calculation was performed according to the following equation:

$$\text{Kilograms of waste solids/acre per year} = \frac{\text{Annual volumetric mean generation} \times \text{Density of waste as applied} \times \text{\% solids in waste}}{\text{Acres of application area}}$$

In those cases where estimates of the waste density and % solids were not available from the waste generator, values obtained from laboratory analysis of waste samples collected during sampling visits to each site were used. As indicated in assumption 2 above, the value of the quantity "acres of application area" in the above equation was equal to the area in acres of the waste application area sampled in this study.

Annual Leading Rate of Individual Waste Species --
The quantity "kilograms of waste solids/acre/year" calculated in Step 1 was multiplied by the concentration in ppm of the element of interest determined in this study in waste samples collected from each site to give the annual loading of that element:

kg/acre/year x mg/kg (=ppm) of element of interest in waste solids = mg/acre/year

According to assumption 3, the waste was assumed to be incorporated uniformly into the top 12 inches of soil over the entire application area so the units of this quantity were assumed to be equal to mg/acre-foot/yr.

Annual Increase of Individual Waste Species --
The annual loading expressed as mg/acre/yr of each element of interest obtained in Step 2 was divided by an estimate of the average mass of one acre-foot of soil to give the predicted annual increase in concentration of each element of interest.*

Estimated Years of Waste Application --

The predicted annual increase in concentration of each element of interest was used to estimate the years of waste application necessary before one could expect to observe any increase above background of the elements analyzed in this study. The latter quantity depends on the detection limits of the sampling and analytical methods used for each element of interest. For example, the atomic absorption spectroscopic procedures used for analysis of many of the elements determined in this study involved digestion of ~1.5 g of soil and dilution of the resulting solution to 50 milliliters. Assuming that our instrumental method was capabile of detecting a change in concentration

---

[The average mass of one acre-foot of soil was calculated as follows:

1 acre ~ 43,560 ft^3; 1 acre-foot =
43,560 ft^3 x 1 ft = 43,560 ft^3;
43,560 ft^3 x .0283 m^3/ft^3 = 1233 m^3;
average bulk density = 1.6 g/cm^3 = 1.6 x 10^3 kg/m^3 (cf. Overcash, M.R. and D. Pal, Design of Land Treatment Systems for Industrial Wastes Theory and Practice, Ann Arbor Science, 1979);
1233 m^3 (1.6 x 10^3 kg/m^3) 2 x 10^3 kg
Therefore,
(mg/acre-foot/yr) ~ 2 x 10^6 kg/acre-foot = $\frac{\text{mg of element of interest}}{\text{kg of soil-year}}$ =

ppm/year]

of the element of interest in that solution equal to 1 part per million, the corresponding concentration change of that element in the soil sample taken for analysis would be ∿ 30 parts per million:

$$\left(\frac{1\mu g}{mL} \times 50\ mL\right) / 1.5\ g \simeq 30\mu g/g = 30\ ppm\ in\ soil$$

The quantity ppm/year calculated in Step 3 was divided by 30 ppm to give the number of years of waste application necessary to observe a concentration change. Note that the "observable concentration changes" referred to here are not the same as "significant concentration increases" referred to in the preceding discussion.

For most elements determined in this study by atomic absorption (AA), the actual instrumental detection limit is probably lower than 1 ppm. However, since a systematic study of the detection limits of the combined sampling and analytical methods was beyond the scope of this study, the 1 ppm estimate may, in fact, be a more reliable estimate of the actual detection limits, given the uncertainty associated with the sampling methods.

Organic Data Interpretation

The principal objective of the organic chemical analysis program was to obtain data for a preliminary evaluation of the effectiveness of land treatment in degrading organic components of chemical wastes. To accomplish this objective it was necessary to characterize the organic components of the waste and to look for evidence of significant accumulation, degradation or migration of those components in the soil.

The organic analysis scheme provided for quantitative analysis of extractable volatile (TCO) and non-volatile (GRAV) organics, and of three polarity classes (LC-H, LC-A and LC-X) by liquid chromatography. Qualitative analysis of the organics by compound type was achieved by HRMS which provided data on heteroatom composition and the degree of compound saturation (R + DB values).

The combined qualitative and quantitative results provide insight into the extent of waste component degradation. For instance, an increase in polar species in APN area samples can be taken as an indication that the aromatic and aliphatic constituents originally in the waste have partially degraded since the byproducts of aerobic oxidation are generally polar oxygenated species. Typically, the organic analysis results do not permit determination of which waste components are being transformed into particular types of degradation products. However, the HRMS data do indicate which specific classes tend to persit in the soil column and which classes tend to appear as degradation products.

Accumulation of certain waste types can be determined by increases of aromatic and aliphatic classes relative to each other. For example, suppose the LC-H and LC-A fractions of extractable organics account for more than 50% of the organics in the APN 0-6 and 6-12 layers and in the control soil in

these fractions are only 10% of the total. The ratio of LC-A to LC-H in the waste is 0.24; in APN 0-6, 0.37 and in APN 6-12, 0.96. The absolute values of the LC-H and LC-A concentrations were lower in the APN 6-12 than in the 0-6. These types of trends are indicative of 1) preferentially degradation/or loss of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) of aliphatic waste constituents over that of aromatic hydrocarbons, and 2) in the APN soil compared to the CTL soil, without the appearance of oxidative degradation.

SECTION 4

RESULTS AND DISCUSSION

WASTE CHARACTERISTICS

Total Mass of Parameters Analyzed

Data for the total amounts of all species determined in samples of waste solids from samples taken at the site in July 1978 are listed below.

Metals	TOC	TKN	SO_4	Cl	Total µg	%
9,918	442,500	81,000	600	14	534,000	53.4

This indicates that species determined in this study account for slightly greater than 50% of dry waste weight. Species not determined that might account for the balance include the elements Fe, H, O, Si, and/or Al. Consideration should be given to the presence of possibly substantial amounts of unidentified species in subsequent interpretations of the analytical data presented.

Inorganic Analysis

The results of analysis for total metals, TOC and TKN, in the waste are presented in Table 4. These data were used along with data obtained from the site owner on waste application rate (2×10^5 gal/yr over 1 acre), waste density as applied (8.5 lbs/gal), and % solids (6.0%) to calculate the years of waste application necessary before one would expect to observe any increase above background in the application area soils of the elements in Table 4. Based on these results, observable increases in the application area at the time of sampling would be expected for C, N, Cr, Ca, and Na (in decreasing order of predicted concentration).

Organic Analysis

Organic analysis was conducted with a slurry of the waste. The waste was found to contain 2200 mg/L of extractable organics. On the basis of the Liquid Chromatography separation of the extract, the organic materials could be characterized as follows:

Aliphatic Hydrocarbons, volatile (TCO):	3.6%
non-volatile (GRAV):	32.0%
Aromatic Hydrocarbons, volatile (TCO)	1.4%
non-volatile (GRAV):	9.0%
Polar Organics, volatile (TCO):	0.5%
non-volatile (GRAV):	54.0%

TABLE 4. INORGANIC WASTE ANALYSIS AND PREDICTED POSSIBLE YEARS OF APPLICATION NECESSARY FOR OBSERVABLE CONCENTRATION INCREASES

Element	Concentration in Waste (µg/g dried solids)	Estimated Years Required for Observable Soil Concentration Change
As	0.6	*
B	2.4	*
C	44.25%	1
Ca	1200.0	1
Cd	2.8	*
Cr	5600.0	1
Cu	14.0	*
K	390.0	3
Mg	360.0	3
Mo	1.1	*
N	8.1%	1
Na	1300.0	1
Ni	1.0	*
P	937.0	2
Pb	54.0	*
Se	< 0.1	*
V	5.2	*
Zn	50.0	*

* = greater than 10 years

The recovery from the LC column for this sample was 76%. The above data have been normalized to 100%. From these results, it appears that the volatile fraction comprises 5.5% of the extract. Only a small quantity of waste can be expected to be lost from the soil due to volatilization.

The results of the High Resolution Mass Spectrometer (HRMS) analysis of the waste extract are presented in the Ring + Double Bond (R + DB) summary matrix (Table 5). The hydrocarbon content of the waste is found, according to ELCOMP data, to include a large molecular weight range (up to 400). The waste contains small quantities of polynuclear aromatic hydrocarbons (PAH), up to five fused rings (R + DB15). The polar components of the waste include C, H, N and C, H, O elemental compositions. The C, H, N species are primarily aromatic (R + DB 5,6 and 7); ELCOMP data show a high molecular weight series ($C_{24}H_{37}N$, $C_{22}H_{35}N$, etc.) dominating this category. The C, H, O species are primarily saturated and unsaturated fatty acids and their ms fragments with 1-4 oxygen atoms per ion, according to ELCOMP. The molecular weight range for these fatty acid materials extends up to about 400. Analogous materials in the control samples have typically not exceeded mw 250 ms fragments. The high molecular weight fatty acids, therefore, may serve as tracers for waste components.

Overall, the site waste can be described as containing low levels of aromatic hydrocarbons, including some PAH, and abundant, relatively high molecular weight, aliphatics (GRAV) and polar organics. Sulfur species were not detected in the waste.

SOIL CHARACTERISTICS

An application area one acre in size which received waste for the first time in 1978 was chosen as the sample area. The choice was based on the availability of a suitable control area with respect to the application area. Roughly 3000 gallons of waste had been incorporated into the soil in this area about 3 months prior to our sampling visit.

Inorganic Analysis

Inorganic analytical data on soils is presented in Table 6. Results for total metals, Total Organic Carbon (TOC), and Total Kjeldahl Nitrogen (TKN), are presented as ratios (APN/CTL) of total concentration in application area to total concentration in control area. As discussed in Section 3, for the purpose of this report, it was judged that a significant change relative to background levels is indicated by a difference in the mean APN area concentration of more than + 20% relative to the mean CTL area concentration (i.e., APN/CTL > 1.2).

At the site, the APN/CTL ratios for Na, C, N, and Cr -- 2.0, 2.2, 2.4, and 23.2, respectively -- indicate that these elements show observable increases in application area soils as was predicted in Table 4. The calculated and observed concentration changes for these three elements are given in Table 7. The predicted and observed concentration increases for these three elements are remarkably close, suggesting that no migration of these elements laterally or to a depth of >12" has occurred. The concentration of Cr in the APN 6-12" sample is greater than the concentration of Cr in the CTL samples. This is consistent with the observation made during sample collection that discrete, clearly iden-

TABLE 5. R + DB SUMMARY MATRIX FOR SITE WASTE SAMPLE*

R + DB	C,H	C,H,N	C,H,O	Total (from HRMS Analysis)
0				0
1	11.1		3.0	14.1
2	17.6		9.6	27.2
3	12.3		14.2	26.5
4	5.7	0.3	3.2	9.2
5	1.2	0.6	1.3	3.1
6	5.3	6.2	0.1	11.6
7	2.1	2.8		4.9
8	0.9	0.5		1.4
9	0.7			0.7
10	0.5			0.5
11	0.2			0.2
12	0.2			0.2
13				
14	0.1			0.1
15	0.1			0.1

*All data in percent, normalized to 100%

tifiable pieces of the waste could be observed in the soil to a depth of about 8 inches. The tilling methods used at this site for waste incorporation are apparently very effective in distributing the waste throughout the top 8" or so of soil.

Inspection of the mean concentration changes for the other elements measured (APN/CTL ratios, Table 6) suggests that apparent increases above background may not yet be significant since all elemental concentrations involved are comparatively low in both control and application area samples. Comparison of APN 0-6" to CTL 0-6" samples only, indicates a generally small but significant increase in a number of elements in the application area surface soils. These include: As, B, Ca, Cd, Cu, Pb, V. Such an observation suggests that the depth at which samples were taken, even in the 12" range sampled here, are important in determining the effects of waste application. Considering the single application and recent disposal level, such an observation could have significant implications for the design of sampling programs. However, given the fact that for most of these elements (Ca is the exception) increases would not be predicted based on waste characterization, and the fact that soil amendments of documented chemical composition are used in undocumented quantities for agronomic purposes, further investigation of this issue is needed.

Data for pH, CEC, sulfate, chloride, and electrical conductivity are given in Table 8. The slight increase in electrical conductivity in the APN 0-6" sample suggests that some portion of the waste components showing significant increases above background are migrating as soluble salts. The increased concentrations of sulfate in the APN area samples support this observation and are consistent with the fact that Cr used in leather tanning is converted in the leather to chromium (III) sulfate. Also, the ratio of Cr to TOC in the waste (.013) is close to the same ratio in the APN 0-6" sample (.031) and both ratios correspond to the amount of Cr which could be expected to be present in chrome-tanned leather.

Organic Analysis

Two control samples -- one composite from 0-6" depth (CTL 0-6) and one composite from 6-12" depth (CTL 6-12) in the control plots at the land treatment site were analyzed, to characterize the extractable organic materials that might be found in a range of natural soils. Table 9 presents data on the total organic carbon content and the quantity of extractable organic material in the site control samples. It is obvious that a small and highly variable portion of the soil organic material is extracted by methylene chloride. Known types of nonextractable organics include high molecular weight polymeric materials, such as amino acids. Non-polar and moderately polar organic species of molecular weights up to 500 or 1000 are generally efficiently extracted from environmental samples by methylene chloride. All of the extracted material is in the GRAV range (b.p. >300°C) which is expected, since TCO range organics (b.p. 100-300°C) would be lost from soil by volatilization. Also expected is the observation that CTL 6-12" samples have considerably lower levels of extractable organics than CTL 0-6" samples (Figures 1, 2, and 3).

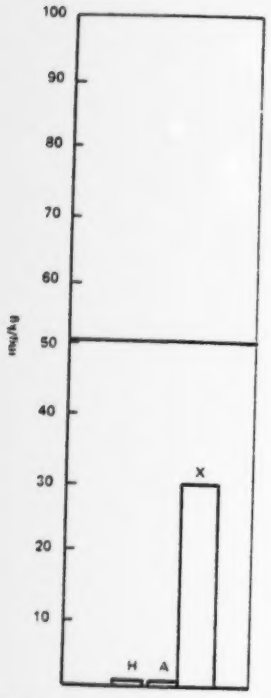


FIGURE 1 LC RESULTS FOR CTL 0-6 SAMPLES

Legend
X – Polar
A – Aromatic
H – Aliphatic

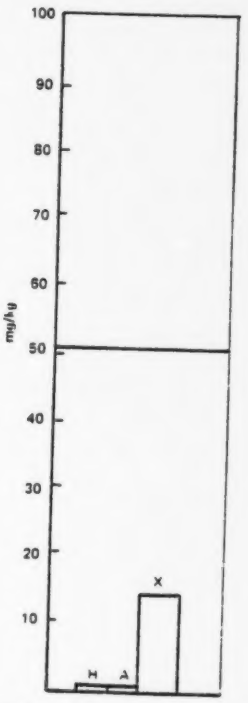
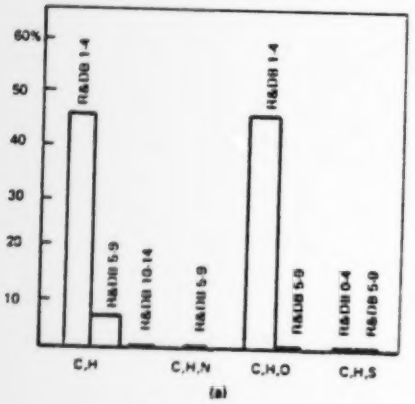


FIGURE 2 LC RESULTS FOR CTL 6-12 SAMPLES



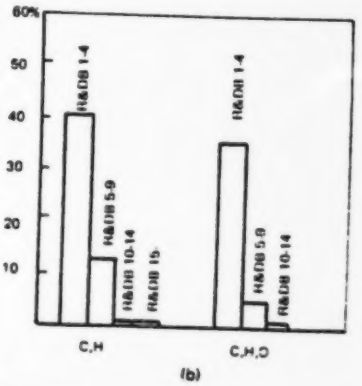


FIGURE 3 (a) COMPARISON OF R&DB CLUSTERS FOR CTL 0-6 SAMPLES
(b) R&DB CLUSTERS FOR CTL 6-12 SAMPLES

TABLE 6. INORGANIC ANALYSIS OF CONTROL AND APPLICATION SOILS

	Concentration in Soils (ug/g) dry wt.				
	CTL		APN		
Element	0-6"	6-12"	0-6"	6-12"	APN/CTL*
As	4	4	11	3	1.8
B	3.0	4.7	13	2.3	2.0
TOC	1.45%	NA	3.19%	NA	2.2
Ca	2200	1700	2900	1700	1.2
Cd	0.3	0.3	0.7	0.3	1.7
Cr	17	8.7	560	37	19.8
Cu	11	11	32	13	2.0
K	2300	3300	620	2200	0.5
Mg	5000	5300	6100	5400	1.1
Mo	2.3	3.3	3.4	2.3	1.0
TKN	0.14%	NA	0.33%	NA	2.4
Na	22	30	85	18	2.0
Ni	16	18	15	13	0.8
P	9700	12000	13000	13000	1.2
Pb	33	23	50	23	1.3
Se	0.3	0.1	0.3	0.2	1.3
V	33	33	57	33	1.4
Zn	87	70	110	80	1.2

NA - Not Analyzed

* = APN/CTL Ratio is calculated by $\left\{APN(0\text{-}6) + APN\ (6\text{-}12)\right\} \Big/ \left\{CTL(0\text{-}6) + CTL\ (6\text{-}12)\right\}$

TABLE 7. CALCULATED AND OBSERVED CONCENTRATION CHANGES IN SITE APPLICATION AREA SOILS

	Element			
	C	Cr	N	Na
Calculated[1]	+1.1 %	+130	+1900	+27
Observed[2]	+ .87%	+250	+ 950	+26

1. Calculated concentration change =

$$\frac{[(\text{Kg solids/acre/yr.}) \times (\text{ppm of element in waste}]}{2 \times 10^6 \text{ kg soil/acre-ft.}}$$

2. Observed mean concentration change =

$$\frac{[(\text{ppm APN 0-6" + APN 6-12"}) - (\text{ppm}_{\text{CTL 0-6" + CTL 6-12"}})]}{2}$$

TABLE 8. SOILS: INORGANIC PARAMTERS

Sample	pH	C.E.C. mg/100g	E.C. µmhos	$SO_4^=$ µg/g	Cl^- µg/g
Waste				600	14
Soil:					
CTL 0-6	6.8	14.2	210	80	4
CTL 6-12	6.8	10.3	165	180	2
APN 0-6	6.0	13.7	310	320	3
APN 6-12	6.5	10.3	123	320	3

TABLE 9. QUANTITIES OF TOTAL AND EXTRACTABLE ORGANIC MATERIAL IN CONTROL SOIL SAMPLES

	Organic Material, mg/kg	
	Total Organic Carbon	Extractable Organic
CTL 0-6"	14,500	45
CTL 6-12"		13

Sufficient similarity exists among the control area soils for this site and three additional land treatment sites to provide a composite picture of a "typical" sample in terms of extractable organics:

> Control soil samples in this project typically contained ≤150 mg/kg of extractable organic material, all in the GRAV range (boiling point >300°C) of which more than 80% is polar. The HRMS matrix analysis approach showed predominantly R + DB 1-4 hydrocarbons and oxygenates, with some R + DB 5-9 hydrocarbons and nitrogenous materials. Little or no material in the R + DB 10 range was present.

This definition of a typical control sample constitutes one general fixed reference point for evaluation of data on application area soil samples. The other reference point is the waste applied to the land treatment site. Significant site-specific details related to the control samples is also discussed as appropriate. However, it seems that the composite control sample description is generally useful and credible--because of its applicability to four sites analyzed for organic composition.

Application Area Soils

The application area 0-6" depth (APN 0-6) and 6-12" depth (APN 6-12) samples were found to contain 500 mg/kg and 51 mg/kg, respectively, of extractable organics. These values are substantially higher than the corresponding levels for the control samples at the site: 45 mg/kg for CTL 0-6 and 13 mg/kg for CTL 6-12. These data imply that there has been a significant accumulation of extractable organic materials in the application area soil samples.

Figure 4 presents the results of the LC separation of the application area samples, as well as those of the corresponding waste and control area samples. It seems clear that one need consider the waste and APN 0-6 samples to evaluate this land treatment process.

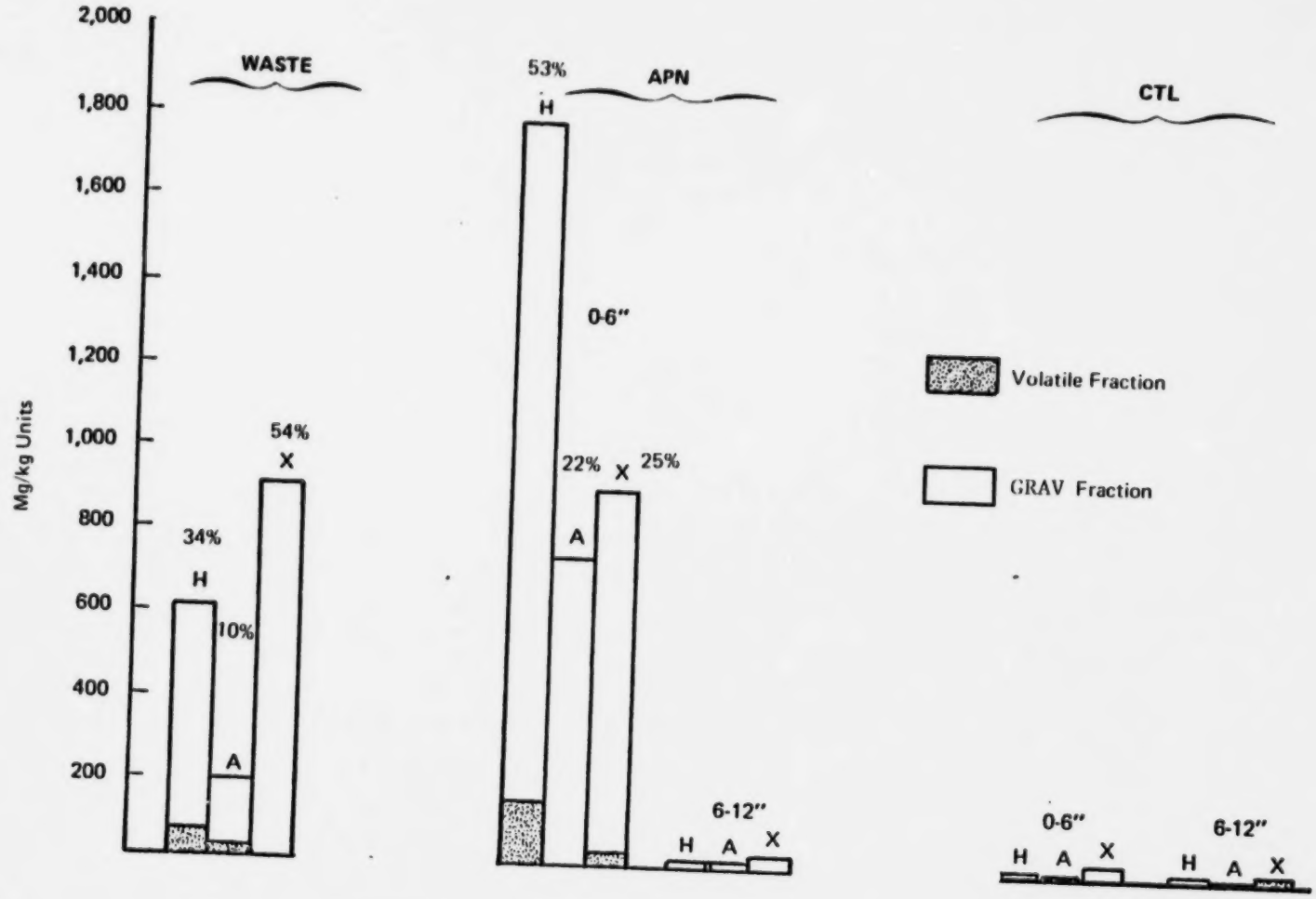


FIGURE 4 SCHEMATIC REPRESENTATION OF LC SEPARATION INTO ALIPHATIC (H), AROMATIC (A) AND POLAR (X) ORGANIC CLASSES.

Comparison of the APN 0-6 and waste sample LC fractionation patterns reveals that the APN 0-6 sample is relatively richer in aliphatic hydrocarbons (LC-H = 53% of total) than is the waste (LC-H = 34% of total). The APN 0-6 sample is also relatively enriched in aromatics (LC-A = 22% vs. 10%) and relatively depleted in polar organics (LC-X - 25% vs. 54%). This shift in the LC fractionation pattern is essentially the opposite of the shift expected to accompany oxidative degradation of the waste components. It is interesting to note that at this site there does not seem to have been extensive preferential loss of volatile TCO range hydrocarbons, which constitute about 9% of LC-H for APN 0-6 vs. about 10% of LC-H for the waste. Taken as a whole, the LC data appear to indicate that waste components are accumulating without undergoing substantial decomposition.

In Figure 5 the R + DB cluster profiles, on a relative distribution basis, are plotted for the waste, APN 0-6, and CTL 0-6 samples. Figure 6 presents similar profiles in which the R + DB data have been weighted to reflect the differences in quantities of extractable materials in the various samples. The cluster profiles confirm the LC fractionation results, in that APN 0-6 is seen to be depleted relative to the wastes in the heteroatom compositions that constitute the polar materials. Examination of the ELCOMP data shows that the C, H material in APN 0-6 includes the same range of high molecular weight hydrocarbons found in the waste; these ions are not present in the CTL 0-6 sample. This is further evidence that waste organic components are accumulating without degradation.

The oxygenated compositions indicated by ELCOMP for the APN 0-6 sample are similar to those for the waste and include high molecular weight (up to C_{18}) fatty acids and related fragment ions. These data do not provide convincing evidence for oxidative decomposition of the waste.

It is not possible to determine whether the apparent relative depletion of C, H, O materials in APN 0-6 is due to some process that selectively removes or degrades those materials. It does appear, however, that the high molecular weight aromatic C, H, N species in the waste are being selectively depleted from the APN 0-6 extract, compared to the waste. The major C, H, N components of the waste were not found in the APN 0-6 HRMS analysis. Together with the apparent depletion in C, H, O material, these data may be indicating that high molecular weight polar organics are not efficiently extracted from the soil. Alternatively, those materials might be selectively degraded.

In summary, the results of the organic analysis of the land treatment samples imply that major waste components have accumulated in the application area soils to an appreciable extent. The data show no evidence of oxidative degradation of waste materials. There is some evidence that high molecular weight polar organic components of the waste (C, H, O and C, H, N species) are either selectively lost or not extractable from the application area samples.

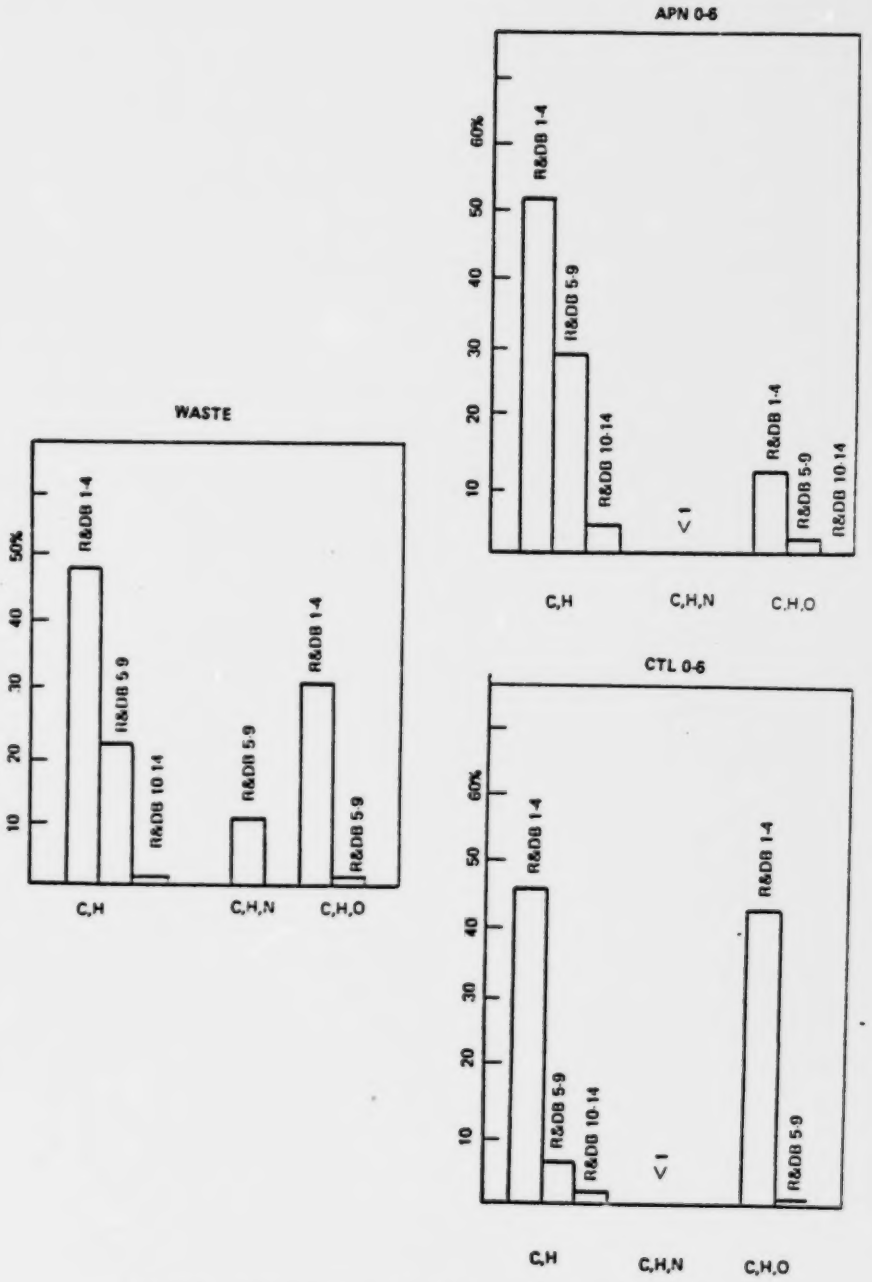


FIGURE 5 R+DB CLUSTER PROFILES, RELATIVE ABUNDANCE BASIS

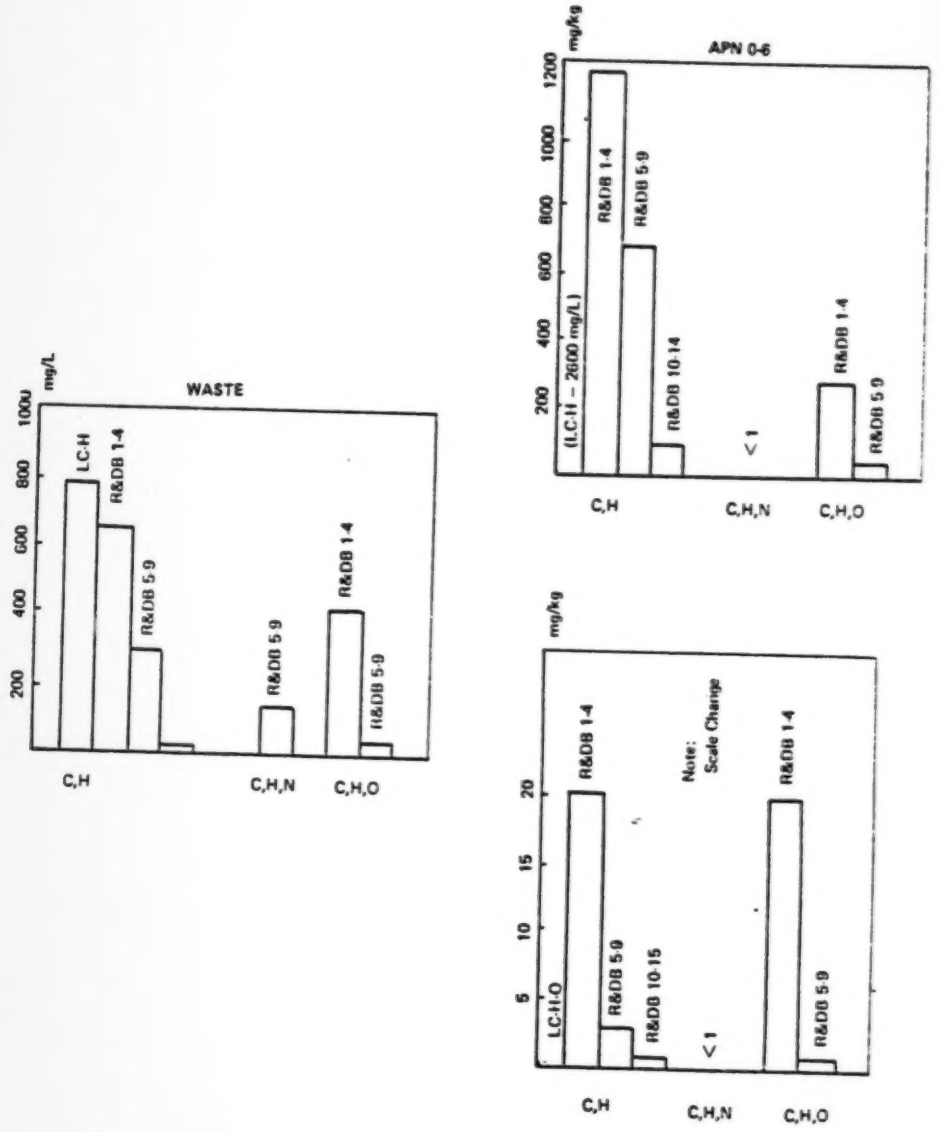


FIGURE 6 R+DB CLUSTER PROFILES, WEIGHTED BASIS

PLANT ANALYSIS

Whole corn plants, above soil level, were collected randomly from within the soil sampling grid at the application area and the control area, with a composite made of samples for each area. For the most part, slight increases observed in elements such as Ca, K, Mg, and Na (Tables 10 and 11) could easily represent normal variations in concentrations of these constituents. The relative increases in Ni and As, while small on an absolute basis, are difficult to attribute to waste applications, as levels of these constituents were very small in the waste. These too could be classified as reasonable variations between the two areas based on a single sampling effort.

The largest single metal addition with this waste is chromium and this is reflected in increased soil levels (Table 7). Further, chromium availability would appear to be higher in application area surface soils based on extractable levels (Table 10). Small increases noted in the chromium content of the application area corn plants could represent Cr enrichment due to waste application, although such increases are not so large as to enable a definitive conclusion.

Most chromium in the soil, or applied with organic wastes (as is true here) is in or rapidly reduced to the Cr^{+3} state as a very insoluble oxide. Hence, it is typically quite unavailable to plants. It has been shown in a number of studies that chromium tends to be concentrated in the roots with relatively less translocated to other parts of the plants (unless extremely high concentrations exist in the soil). Roots of corn crops at the site were not sampled and any further monitoring of that site should consider roots.

TABLE 10. PLANT SAMPLE CONTENT OF TOTAL ELEMENTS AS ANALYZED IN ASHED SAMPLES

Element	Concentration (ug/g) ash	
	CTL	APN
Ash	5.9	3.8
As	1	3
B	59	56
Ca	4.4%	5.0%
Cd	3	2
Cr	21	21
Cu	69	70
K	10.0%	11.7%
Mg	3.5%	4.6%
Mo	13	12
Na	940	1400
Ni	7	16
P	1.9%	1.5%
Pb	51	63
Se	0.5	0.5
V	5	4
Zn	690	690

TABLE 11. SOIL SAMPLES: DTPA EXTRACTABLE METALS

	Concentration (µg/g)			
	CTL		APN	
Element	0-6"	6-12"	0-6"	6-12"
As	NA	NA	NA	NA
B	0.2	0.2	0.1	0.1
CA	NA	NA	NA	NA
Cd	<.1	<.1	0.1	<.1
Cr	<.1	<.1	1	0.1
Cu	<.1	1	3	3
K	22	4	31	14
Mg	62	30	55	21
Mo	<.1	<.1	<.1	<.1
Na	11	12	12	12
Ni	2	1	2	1
P	54	38	48	37
Pb	--	--	--	--
Se	NA	NA	NA	NA
V	0.1	0.1	0.1	<.1
Zn	4	1	5	2

APPENDIX

METHODS OF SAMPLING AND ANALYSIS

DATA COLLECTION PROCEDURES

Several approaches were used to collect data from the six field sites selected for study. Information sources included published surveys such as those produced by the Soil Conservation Service and/or local universities and state agencies. Where feasible, information gathered from interviews with site or industry personnel along with site observations were utilized to confirm or adjust such information for location specificity.

FIELD SAMPLING

The field sampling and analysis program was designed to provide information on the following:

1. The rate and extent of waste degradation,
2. The migration of inorganic species,
3. The accumulation of waste constituents in the soil, and
4. Bioaccumulation of inorganic species in vegetation.

To this end, measurements were made of the concentration of various chemical species in soil and vegetation samples taken from waste application and control areas. The species selected for analysis were those that occur as a direct result of the land cultivation operation and/or transport of any constituents of the wastes.

Sampling Methods

Sampling Locations--

At each site, samples were taken from (1) the area where waste had been applied and (2) the best identifiable control area. The ideal control area would have been upwind and upgradient of the waste application area, but in all other respects would have been identical to that area except that no waste had been applied. Selection of an appropriate control area was a problem at the majority of sites for a variety of reasons. In general, the design and operation of most sites did not include provision for a bona fide control area as described above. More specifically, problems included substantial variations in soil characteristics, drainage patterns and vegetation occurring within small distances; and uncertainty about the history of waste application outside the boundaries of the present application site. In all cases, a "control" area

was selected which necessitated the least compromise in the requirements stated above. In both control and application areas, samples were collected from a 4 x 4 grid covering the area. Wastes were collected from storage facilities or other sources, selected so as to assure that the samples were representative of the waste that was actually applied.

Sample Types--

The types and numbers of samples collected at each site included at a minimum the following:

		Control Area	Application Area
1)	Waste	1 Sample	
2)	Soil	2 Samples	2 Samples
3)	Soil-Waste Mixture	--	2 Samples
4)	Vegetation	1 Sample	1 Sample

Core samples of soil and soil-waste mixture were taken with a sampling tube. The resulting cores were 1" in diameter and 12" in length. These samples were divided in the field into two subsamples corresponding to 0-6" soil depth and 6-12" soil depth. Bulk samples were subsequently coned, quartered, and riffled to obtain amounts of sample appropriate for each analysis. Vegetation samples were collected from the same control and application areas from which soil samples were obtained. Unless noted otherwise, composite vegetation samples were prepared from whole plants minus roots. There were no opportunities for sampling surface water, runoff, or groundwater at any site during the sampling visits made.

CHEMICAL ANALYSIS

Inorganic

Analyses of inorganic parameters were conducted on the waste samples, soil and soil-waste mixture composite samples from application and control areas, and vegetation composite samples from application and control areas. Analytical methods used for determination of inorganic parameters are shown below. DTPA-Extractable metals are those metals which may be available for biological uptake.

Parameter	Method
B, Cu, Cd, Cr, Cu, K	HNO_3-$HClO_4$ digestion, plasma emission spectroscopy
Mg, Mo, Na, Ni, P, Pb, V, Zn	
As, Se	Hydride evolution, atomic absorption spectroscopy

Total Organic Carbon (TOC)	Combustion, gravimetric
Total Kjeldahl Nitrogen (TKN)	Digestion, distillation, volumetric
Sulfate	0.1 M LiCl extraction, ion chromatography
Chloride	H_2O extraction, volumetric $Hg(NO_3)_2$ titration
Cation Exchange Capacity (CEC)	Volumetric
Electrical Conductivity (EC)	Conductivity Meter
pH	pH Meter
DTPA-extractable metals	DTPA extraction, plasma emission spectroscopy

Organic

The organic analysis scheme is shown schematically in Figure 7. The methodology involved:

1. Solvent extraction with methylene chloride;
2. Quantitative analysis of volatile and non-volatile organics;
3. Liquid chromatographic separation of the extracts to divide the organics into three polarity classes: aliphatic hydrocarbons, aromatic hydrocarbons, and polar species; and
4. Qualitative analysis of organic compound classes present by high resolution mass spectrometry.

Each of the steps of the methodology is described in further detail below.

Extraction--

The method adopted for isolation of organic components from the waste and soil samples was extraction with methylene chloride. Methylene chloride is a solvent which gives high extraction efficiency for a wide range of organic compound types. In particular, it is generally effective for non-polar and moderately polar, hydrophobic organics, which are the types of compounds that dominate many current lists of compounds of concern. It should be recognized, however, that polymeric, humic, proteinaceous materials, very polar, water-soluble, or soil-bound species will not be efficiently extracted. It should also be noted that these non-extractable species, if isolated, would generally not be amenable to available analysis techniques. An organic compound which is extractable from a waste sample may not be extractable from a corresponding soil sample because of soil bonding. Since non-extractable organics are probably less likely to be transported into plant cells, they may be of less environmental concern.

Control and application area soil samples (ca 100 g) were Soxhlet extracted with methylene chloride (ca 200 mL) for 24 hours. Waste samples were

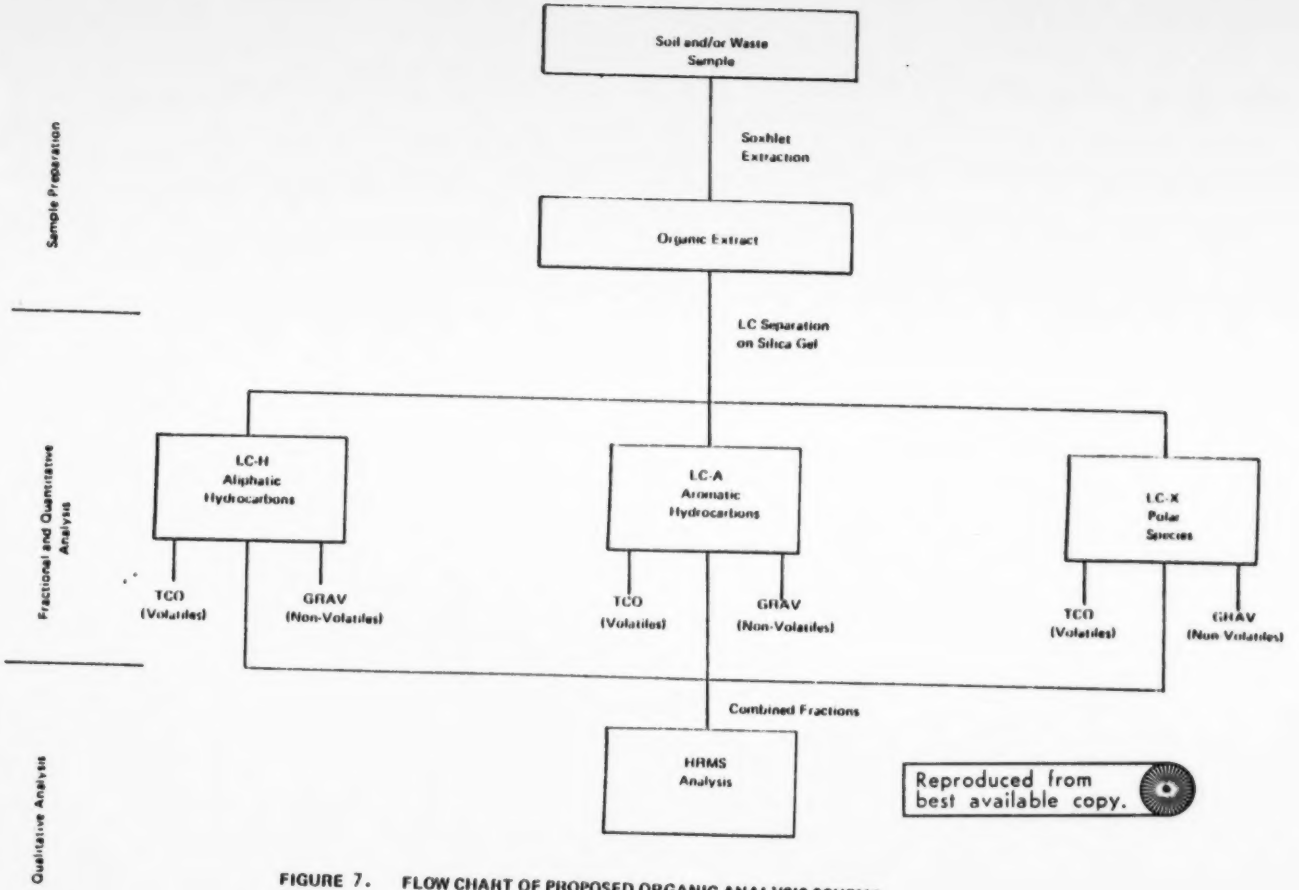


FIGURE 7. FLOW CHART OF PROPOSED ORGANIC ANALYSIS SCHEME

subjected to Soxhlet extraction, or to liquid-liquid separatory funnel extraction (3 times 100 mL of solvent per liter of waste), depending on their physical state. The methylene chloride extracts were concentrated to 10 mL final volume by use of Kuderna-Danish evaporative concentrators.

Quantitative Analysis--

Total Chromatographable Organics (TCO)--The Total Chromatographable Organics (TCO) analysis is a gas chromatographic (GC) analysis procedure that uses a flame ionization detector. A 1-5μL aliquot of the sample is injected. Resolution of individual QC peaks is not intended. The total integrated detector response is used to derive a single estimate (mg) of the quantity of material in the 100-300°C boiling point range.* The detection limit for a complex sample mixture is on the order of 50 ppm (w/v) in the solution injected. This corresponds to 0.5 mg total in the 10 mL sample extract.

Gravimetric Analysis (GRAV)--The GRAV procedure is a quantitative analysis of non-volatile components (materials above 300° boiling point range) of the sample extract. An aliquot of the organic solution is evaporated to constant weight, over silica gel, in a tared weighing dish. The practical detection limit is on the order of 0.1 mg in the 1 mL sample taken for GRAV analysis. This corresponds to 1 mg total in the 10 mL sample extract.

Liquid Chromatographic Separation--

A liquid chromatographic (LC) separation on silica gel was used to separate the extracted organics according to polarity. This is a lowresolution technique that has been demonstrated at Arthur D. Little, Inc. to provide reliable separation of organic components into three classes as indicated below.

LC-H: Aliphatic Hydrocarbons

LC-A: Aromatic Hydrocarbons

LC-X: Polar Organics (oxygenates, amines, etc.)

Details of preparation of the silica gel LC column have been published. The methylene chloride extracts were applied to the column after solvent exchange into cyclohexane. The elution sequence used in this program was as follows:

LC-H: 15 mL of pentane

LC-A: 15 mL each, sequentially, of 20% methylene chloride in pentane; 50% methylene chloride in pentane; and methylene chloride

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* Arthur D. Little, Inc., studies using model compounds have shown that n-hexadecane (b.p. 303 C) defines a reasonable break point between TCO and GRAV range materials.

LC-X: 5 mL each, sequentially, of 5% methanol in methylene chloride; 20% methanol in methylene chloride, and 50% methanol in methylene chloride.

Each fraction was analyzed by TCO and TRAV procedures as described above. The fractions were then recombined prior to HRMS analysis.

The LC procedure was originally scaled for 15-100 mg samples applied on column. However, the total amount of material available for some samples in this program was 10 mg. Quantitative recovery from the column was 70-100% when samples containing about 10 mg or more were used, but 50% for very small samples.

The reproducibility of the extraction and LC separation for these samples was checked by running duplicate LC columns on a site application area soil extract. The results are shown in Table 12.

High Resolution Mass Spectrometry--

High resolution mass spectra were obtained on the recombined LC fractions for each of the landfarm sample extracts. A Dupont (CEC) 21-110 B high resolution mass spectrometer, using a glass inlet and solids probe for sample introduction, was employed. Spectra were recorded on photoplates. The basic spectral data were then obtained by a photoplate reader and the position and intensity of the lines transferred directly to a laboratory data system (LDS). This is the HIRES output. The LDS, based on a Data General Elipse S/200 computer, was used for subsequent HRMS data processing.

The high resolution mass spectrometer is capable of measuring masses of ions in the spectrum with an accuracy of better than 0.001 atomic mass unit. Data from the HRMS analysis are reported to four decimal places in m/e (mass-to-charge ratio). The high accuracy and precision makes it possible to take advantage of the mass defect characteristics of atoms and use their exact masses to compute elemental composition assignments for the observed ions. The theoretical mass can be calculated for all "plausible" combinations of elements corresponding to a given mass. "Plausible" combinations are defined by the analyst, based on a preliminary manual examination of the HIRES data. The objective is to allow all of the elemental compositions (C + H; C + H + S; C + H + Cl, etc.) that are necessary to characterize the range of the sample chemistry, but to minimize the computation time and the number of incorrect, "near-miss" match assignments. The theoretical and measured masses are next compared and a "match" is identified when they agree to within a specified value, typically 0.002 or 0.003 atomic mass units. This information constitutes the ELCOMP output.

The ELCOMP output listing normally includes 400 to 1000 lines detected in the spectrum, their intensities, and 500 to 2000 associated chemical composition data. The approach used for interpreting this large quantity of data was to sort the assigned elemental composition into classes according to heteroatom composition (i.e., C,H; C,H,O; C,H,N; C,H,S) and degree of hydrogen unsaturation indicated by rings and double bonds. The R + DB value provides a convenient means of organizing data into probable chemical compound categories. Some examples will illustrate this point:

TABLE 12. REPLICATE EXTRACTIONS AND LC SEPARATIONS ON A SITE SOIL SAMPLE

	% Water	Dry Wt. Extracted (kg)	Extract TCO (mg)	Extract GRAV (mg)	Extract Total (mg)	Total (mg/kg)
Before LC Fractionation						
Sample 1: APN 0-6	15.9	0.0966	ND	9.0	9.0	93.2
Sample 2: APN 0-6	15.6	0.1090	ND	8.0	8.0	73.4
After LC Fractionation						
Sample 1: APN 0-6						
LC-H			0.82	1.67	2.49	25.8
LC-A			0.39	1.17	1.56	16.1
LC-X			ND	4.00	4.00	41.4
						83.3
Sample 2: APN 0-6						
LC-H			ND	1.17	1.17	10.7
LC-A			1.30	0.50	1.70	15.6
LC-X			ND	5.30	5.30	48.6
						74.9

for an n-paraffin, C_6H_{14}, R + DB = 0

for phenol, C_6H_6O, R + DB = 4

for benzothiophene, C_6H_6S, R + DB = 6

for anthracene, $C_{14}H_{10}$, R + DB = 10

for benzopyrene, $C_{20}H_{12}$, R + DB = 15

All paraffins or other saturated species such as acyclic alcohols and sulfides will always be in R + DB group 0. A species must have an R + DB value of 4 or more to be aromatic, and R + DB value of 7 or more to be a naphthalene, an R + DB value of 8 or more to be a polychlorinated biphenyl (PCB), and so on. The R + DB values were grouped in this report as follows: R + DB = 0, 1 R + DB 4; 5 R + DB 9; 10 R + DB 14; and 15 R + DB.

Similar calculations can be made for any species of interest. This approach does not differentiate among the different isomers of any compound class, such as anthracene and phenanthrene, in R + DB 10.

The R + DB and elemental composition values were then used to sort all of the data from HRMS analysis into a compact matrix first according to the R + DB value and second according to the elemental composition of each of the ions identified. This approach presents a simple view of the overall composition of a sample from a highly complex spectrum. This approach requires that all ions finally included in the matrix are parent (molecular) ions. However, a large number of fragment ions in the spectra complicates the analysis. In interpreting the HRMS data it is also necessary to account for isotope ions (e.g., ^{13}C and ^{37}Cl), and composition assignments with large experimental errors. Consequently, in developing the R + DB matrix, certain restrictions were applied in an attempt to eliminate interferences and questionable calculated compositions. The restrictions applied were:

Molecular Weight: Ions below 90 atomix mass units were excluded to minimize the interference from fragment ions.

Error: Calculated compositions which differed from measured values by more than 2 millimass units were excluded.

Isotopes: All calculated compositions that included isotopes such as ^{13}C, ^{34}S, and ^{37}Cl were excluded.

R + DB: Only compositions with integral R + DB values were included, thus excluding fractional R + DB values which arise from fragment ions.

Carbon No.: A minimum carbon number limit was set for each R + DB class.

For this report, the individual intensities of all ions within each R + DB and element group were summed to give a single estimate of the abundance of that group. For each composite sample, these estimates were subsequently displayed in a condensed form as shown in Figure 8.

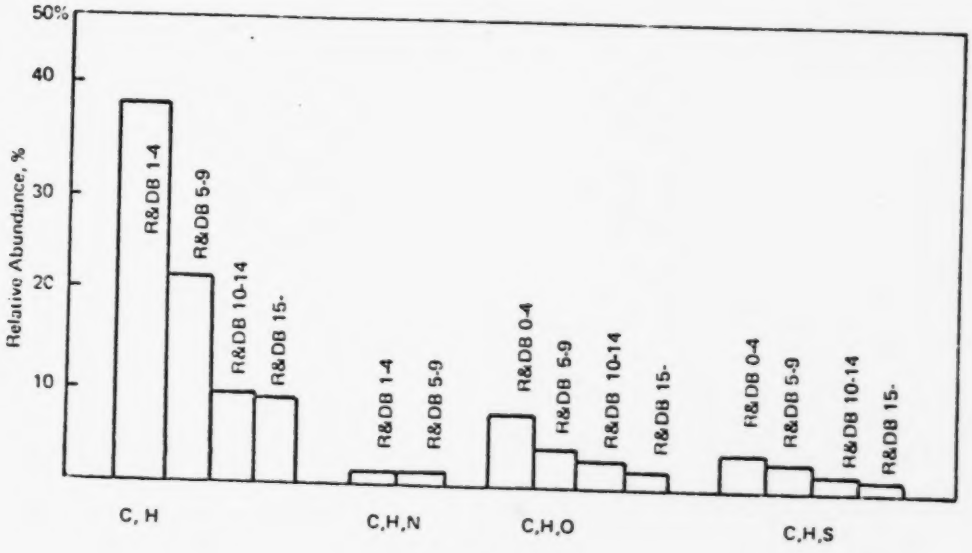

FIGURE 8. EXAMPLE OF DISPLAY OF R&DB AND ELEMENTAL COMPOSITION GROUPINGS FOR A SOIL SAMPLE EXTRACT